STANFORD UNIVERSITY LIBRARY
DEC 6 1915

The University of Washington
Department of Chemistry

A Study of the Factors Influencing the Anodic Passivity of Iron With Notes on Polarization Potentials

BY

SETH CHAPIN LANGDON

A Thesis Submitted in Partial Fulfilment of the Requirements for the Degree of Doctor of Philosophy

U. of Washington

SEATTLE, WASHINGTON:
H. C. PIGOTT PRINTING CONCERN
1915

3781
W31L
UNCLASSED
STANFORD UNIVERSITY LIBRARIES
WITHDRAWN

The University of Washington
Department of Chemistry

A Study of the Factors Influencing the Anodic Passivity of Iron With Notes on Polarization Potentials

BY

SETH CHAPIN LANGDON

A Thesis Submitted in Partial Fulfilment of the Requirements for the Degree of Doctor of Philosophy

SEATTLE, WASHINGTON:
H. C. PIGOTT PRINTING CONCERN
1915

TO

MY BROTHER

—S. C. L.

A STUDY OF THE FACTORS INFLUENCING THE ANODIC PASSIVITY OF IRON WITH NOTES ON POLARIZATION POTENTIALS.

Since the discovery of the passivity of iron by James Keir*[1] in 1790, a very great number of investigations have been devoted to it and allied phenomena. The literature up to the last six or seven years has been reviewed both by Byers[2] and by Heathcote[3]. Most of the more recent work is summarized in the symposium, "The Passivity of Metals," published by the Faraday Society as a report of a meeting held in London, November 12, 1913. This session was attended by many of those interested in passivity, who indulged in a general discussion of the subject both from the experimental and theoretical sides. The appended bibliography† covers the contributions not included in the above mentioned summaries.

A discussion of some of the fact of passivity and of the related theoretical considerations, will be found at the close of the experimental part. Meanwhile, it will suffice to take up the development which led to the investigations herein to be detailed. In the review by Byers

† Lebedev, Zeit. Elektrochem., **18**, 891.
Byers and Vorhis, J. Am. Ch. Coc., **34**, 1368.
MacLeod-Brown, Chem. News, **107**, 15.
F. Flade and H. Koch, Z. Electrochem., **18**, 335-8. J. Soc. Ch. Ind., **31**, 493.
N. Isgarisheb, Z. Electrochem, **19**, 491-498.
Grube, Z. Electrochem., **18**, 189-211. J. Ch. Soc., 102, II, 424.
Dunstan & Hill, J. Chem. Soc. 99, 1853, Proc. Chem. Soc. 27, 222.
Grave, Zeit physik. Chem., 77, 513.
V. A. Kistayakoskii, J. Chem. Soc. 100, II, 401. Seventh International Congress Applied Chemistry, 1909 (Sec. X) 56.
J. A. N. Friend, J. Ch. Soc., 101, 50-6 Proc., 26, 311.
Flade, Z. Physik. Chem. 76, 513.
Muller, W. J., Z. Electrochem., 15, 696. Zeit. physik. Chem., 69, 460.
P. Krassa, Z. Electrochem., 14, 607.
Rudolph Ruer, Z. Electrochem., 14, 633.
Trans. Faraday Society, 1914. Symposium "The Passivity of Metals."
Armstrong, Soc. Chem. Ind., 32, 391.
Smits, Verslag. K. Skad. Weterschappen, 21, 1132.
Brunet, Rev. gen. chem., 17, 66.
Fr. Flade and H. Koch, 88, 307.

* The numbers after author's name refer to a reference list at the close of the paper.

it was pointed out that none of the numerous suggestions as to the cause of passivity were satisfactory, and an attempt was made to define the term which by reason of extension to similar phenomena had become confused. The term was defined as properly applied to an element when it shows "Abnormal electro chemical relations and a chemical inactivity not corresponding to its position in the electro motive series of the elements." It was here also stated, that in oxygen electrolytes the occurence of the passivity in iron, used as an anode, depended upon the condition and previous treatment of the iron, the nature and concentration of the electrolyte, the temperature, the current density, and the time of flow of the current.

In a paper by Byers and Darrin[4] in 1910 it was shown, with various electrolytes, that when the cell containing an iron anode was placed in a strong magnetic field the current density required to render the iron passive was increased, that is, in a magnetic field an iron anode was more difficulty passivified. In a contribution published one year later by Byers and Morgan[5], the same was shown to be true for nickel anodes. In the above outlined work the results failed to check accurately, and this was attributed to the rise of temperature due to heating of the magnet or to mechanical difficulties due to the form of apparatus. Also it was suggested that perhaps other unknown variables prevented exact duplication of results, so that the work, while it clearly showed the trend of facts, was qualitative in its nature.

This research was primarily undertaken to verify the work previously done and since a more powerful magnet with a water cooling device, was available, it was expected that more uniform results could be obtained. Also this subject was considered of particular interest because of the apparent connection between a chemical reaction and the influence of the magnetic field. A search of the literature had revealed not a single authentic case where any direct chemical effect could be demonstrated to be due to a magnetic field. A bibliography of the literature on this subject is to be found in a paper published by Byers and Langdon in 1913[6].

The prosecution of the work led naturally to certain developments connected with passivity in its relations to gases dissolved in the electrolyte and to the potentials developed by iron anodes. The experimental results are therefore detailed under three heads:

I. The Magnetic Field as Related to Passivity, II. Dissovled Oxygen as Related to Passivity, III. The Bearing of Electrode Potential on Passivity.

I. THE MAGNETIC FIELD AS RELATED TO PASSIVITY.

The arrangement of the apparatus used in the first series of experiments is shown in Fig. 1, and consisted of a short test tube, containing the electrolyte, 0.5 N solution of sulfuric acid, supported between the poles of a Weiss magnet capable of furnishing 36000 gauss. The anode was a piece of iron wire, diameter 0.72 mm., sealed in a glass tube with paraffin so that exactly 4 mm. was exposed. The cathode was a platinum wire exposing an equal area. The electrodes were connected in a series with five U. S. storage batteries, a resistance box with a range from 0.1 to 1000 ohms and a Weston milliammeter. A voltmeter, as a shunt, with a key connected the electrodes.

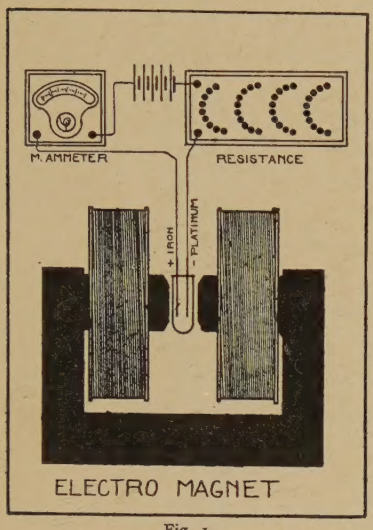

Fig. 1.

At the beginning of each experiment, iron anode was active. As rapidly as possible the resistance was diminished and the current required for the change to the passive condition determined. The change is characterized by a sharp rise in the potential difference, as shown by the voltmeter, a change in the appearance of the iron, an evolution of oxygen, and a drop in the current shown on the milliameter. The "critical" current noted in the accompanying Table I is that which produces these changes within ten seconds after the imposition of a given current. These results are given for various samples of wire, numbered separately, and with various strengths of magnetic field. The results as tabulated show clearly the rise of "critical" current with field strength and the general character of the curve is shown in Fig. 2.

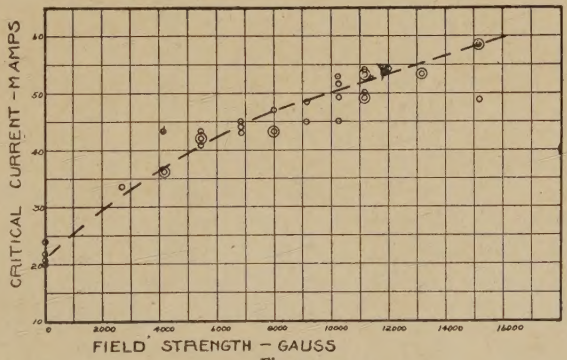

Fig. 2.

TABLE I.

No.	Critical current, M. amps.	Field strength, Gauss.
1a	20	0
1b	24	0
3a	21	0
8a	22	0
3b	33	2700
1c	43	4100
3c	36	4100
5e	36	4100
7e	43	5500
9d	41	5500
10a	42	5500
10c	42	5500
3e	43	6800
6d	45	6800
6e	44	6800
4c	43	8000
4d	43	8000
10d	47	8000
2d	45	9200
4e	48	9200
2e	49	10300
5a	45	10300
6a	49	10300
6b	52	10300
6c	53	10300
9a	49	11200
9b	53	11200
9c	54	11200
11a	53	11200
11b	49	11200
11c	50	11200
5b	54	12000
7d	53	13200
8d	53	13200
7a	48	15200
7b	58	15200
7c	58	15200

During the progress of these experiments it was noted that *stirring of the electrolyte was produced when in the magnetic field* and without carrying the field strengths to a greater intensity the effort was made to determine if this agitation of the electrolyte by the field had any bearing on the delay in the establishment of the passive condition. This is important also because of the extremely divergent views of Fredenhagen[7] and of Grave[8]. The former, supported by many of the investigators, viewing the establishment of passivity as coincident with saturation of iron with occluded oxygen, the latter as simultaneous with complete removal of occluded hydrogen. It was thought that perhaps stirring the electrolyte with various gases would throw light upon both of these questions.

The results were of a character which led to the tentative conclusion that the effects shown by the magnetic field were wholly due to the stirring set up thereby and consequently the stirring experiments were extended to the use of a water motor, giving a slow mechanical stirring, and an electric motor giving a rapid motion. The stirring with gases was produced by delivering the gas into the electrolyte, from below and on both sides of the anode through a double nozzle jet.

Hydrogen from a Kipp generator was supplied at a low pressure with consequent moderate stirring effect. The air and also nitrogen were furnished under small hydrostatic pressure, which was not the same in the two different gases, and the oxygen from a pressure cylinder. The violence of the stirring was, therefore, greatest with oxygen. The motor stirring was produced by using a rotating anode and to determine if the type of motion were important the motor was geared with an eccentric so as to produce a rapid perpendicular motion of the anode. The results of these various stirring effects are given in tabular form in Table II and for comparison the effect of a magnetic

TABLE II.

	1		2		3		4		5		6		7		8	
			H_2		N_2		Air.		O_2		Water		Electric		Eccentric	
No stirring.																
No field.		F.		F.		F.		F.		F.	Motor	F.	Motor.	F.		F.
	20	42	43	57	48	60	50	67	63	67	55	70	93	95	112	117
	22	48	42	62	48	68	58	72	76	77	61	96	104	83	97	95
	21	47.5	41	58	56	70	67	70	77	68	53	92	85	97	97	88
	20	40	54	67	57	63	68	60	80	58	55	75	97	102	91	93
Mean:	21	44	45	61	53	65	61	70	74	74	56	83	95	94	99	98

field of 12,000 gauss intensity without stirring and coincident with stirring is given. Also in Column 1 the critical current without the field is given. The right hand set of figures in each column shows the critical current in the field.

It will be noted that the magnetic field retards the establishment of the passivity, as indicated by the larger critical densities shown under F in column 1. Agitation of the electrolyte also produces retardation as shown in the left hand columns in 2 to 8 inclusive, and the more violent and effective stirring the greater the retardation. It will be noted also that the field increased the effect of the agitations of

lesser violence but the increased violence of stirring, the "field stirring" produces a decreasingly additional effect until with the electric motor and eccentric no influence of the field is apparent. It seems to be conclusive therefore that the magnetic field offers resistance to the establishment of passivity simply because of the stirring effect which it produces upon the electrolyte when undergoing electrolysis, which stirring is visible in a strong magnetic field through the violent agitation of the bubbles of liberated gases.

The stirring of an electrolyte during electrolysis was first noted by Hurnuzescu[9] in 1895. Ashcroft[10] in 1905 obtaind a patent upon stirring fused electrolytes by a magnetic field. In 1907, Frary[11] made application of Ashcroft's method to the rapid deposition of metals by electrolysis, substituting the magnetic field for rotation.

As additional evidence bearing upon this conclusion the rate of rotation of the anode was measured and the corresponding critical current determined. The results are given in Table III.

Here again as in Table I the numbers refer to a given anode and the letters to the different experiments with each. These data are graphically represented in Fig. 3. The variable results obtained are

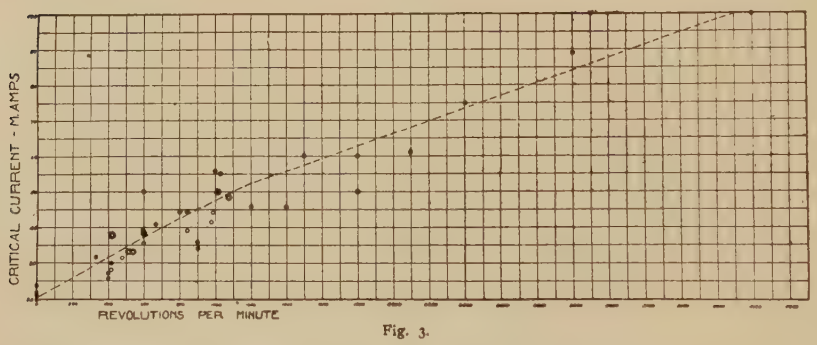

Fig. 3.

not important as bearing upon the conclusion because of the factors which are not under exact control. It will be evident that the stirring effect of a magnetic field will vary with the position of the anode in the field and with any deviation from the perpendicular, which interferes with symmetrical stirring. The experiments were all at room temperature, which of course, is variable to some extent. The wire anodes used, when partially dissolved were flattened on the sides, so that the resulting sharp edges were in the direction of the lines of force of the field. In the stirring by motor the results vary also within limits and these variations are to be ascribed not only to changes

TABLE III.

No.	Critical current	R. P. M.
1a Table I	20	0
1b Table I	24	0
3a Table I	21	0
8a Table I	22	0
4d	32	330
2a	26	400
2b	27	400
8b	38	420
8a	30	420
8c	38	420
9a	38	420
1d	28	420
1c	32	480
7c	33	510
9b	33	510
4c	33	540
8d	33	540
1a	37	600
1b	37	600
3b	50	600
9c	36	600
9d	38	600
4b	41	660
3c	44	800
10d	44	840
6a	39	840
2c	34	900
2d	36	900
6b	42	980
6c	44	990
3a	56	1000
10a	50	1020
10b	50	1020
11a	55	1040
7a	47	1080
7b	47	1080
6d	46	1200
5a	46	1400
10c	60	1500
2e	50	1800
4a	61	2100
11b	75	2400
11c	89	3000
11d	100	4000

in the rate during a given experiment but the stirring by a given rate of rotation also depends upon variation from exact axial rotation.

A comparison of Figures 2 and 3 shows the approximate ratio between the effect produced by the field and that due to rotation of the anode, to be about ten to one, that is, ten gauss produced the same effect as one revolution per minute. This ratio would of course vary with the form of the apparatus.

Explanation of the cause of stirring of an electrolyte by the magnetic field are offered by Drude[12] and by Urbasch[13] but it does not seem to be anything more complicated than the tendency of the movable part of an electric circuit to enclose the greatest possible number of lines of force and since the circuit is closed through a liquid the motion is the tendency of the liquid part of the circuit to adjust itself to the field in accordance with this well established principle.

The retardation of the passive state by the field appears to be independent of the position of the anode with respect to the lines of force. This is shown by the results, obtained in a field of 12,000 gauss, given in Table IV.

TABLE IV.

	Anode perpendicular to lines of force. Critical current.	Anode parallel to lines of force. Critical current.
1	42 m. amp.	44 m. amp.
2	48 m. amp.	40 m. amp.
3	47 m. amp.	46 m. amp.
4	40 m. amp.	46 m. amp.
Mean	44.3	43.5

The result seems striking in view of Remsen's observation that a difference of electromotive force is established between two iron rods in a magnetic field when parallel but not when perpendicular to the lines of force.

The previous observations[2] that the passivity once established is maintained by a minimal current that the passivity is not destroyed by a magnetic field[4] are confirmed. For example iron passive in 0.5 N sulfuric acid solution and kept in that condition by a current of 4.5 milliamperes remains passive when placed in a field of upwards of 20,000 gauss. This was unexpected in view of the results recorded by Nichols and Franklin[14].

These experiments then show that the magnetic field retards the establishment of the passive state in iron and nickel anodes because of the stirring produced by the field in the liquids undergoing electrolysis. The effect is exactly duplicated by mechanical stirring produced either by gases bubbled through the liquid or by motion of the electrode itself. Thus a *sixth factor, that of motion of the electrolyte* may be added to the list, already given, of conditions that influence the establishment of the anodic passivity of iron.

The variation of results, as clearly shown in Figures 2 and 3 indicated that, as yet, the results obtained were qualitative in character,

but it was thought that perhaps the list of variables was complete and that light could be thrown on the subject by experiments in which *two factors were allowed to vary mutually while the other four were held* constant. Below is given, briefly, the experimental methods employed and typical results obtained when the attempt was made to determine the relations between current density and the time required to induce passivity. It was found that it was not necessary to use a mechanical device to produce uniform stirring for, by the method of uniform procedure, as pointed out below, the stirring effect introduced was practically the same in all cases and so could be neglected. The apparatus used was similar to that shown in Figure I except that the magnet was not used and the length of iron wire exposed was 10 mm. instead of 5 mm.

The experimental procedure is outlined below. The external resistance was first adjusted so that a current of the required density would flow through the circuit, and the time required to convert an active anode to the passive condition was determined by a stop-watch, the time recorded being the interval between the closing of the key and the appearance of the phenomena previously described. If the current was not too small, the time required was fairly small, and therefore, iron was dissolved to an extent insufficient to materially affect the diameter of the wire. It was, therefore, possible to make a series of determinations on one section of wire. In order that these should be comparable the circuit was broken as soon as the iron had become passive and the cell was given a vigorous shake. Then after thirty seconds the circuit was closed again for the next determination. This interval renders the effect of stirring uniform and is quite sufficient, for in 0.2 sulfuric acid iron, passive as an anode, almost instantly becomes active when the current is stopped. The character of the results is shown in Table V.

TABLE V.

0.2 N H_2SO_4; temperature, 0°; 10 mm. wire exposed.

Milliamperes current.	Time in seconds to passivify the iron.	Diameter of the wire.
30	12	0.709
30	22	0.707
30	24	0.705
30	26	0.703
30	25	0.797
30	28	0.695
30	28	0.693
30	30	0.687
30	29	0.685
30	29	0.680
30	38	0.675
30	31	0.670

Disrgarding the first determination, there is a range of difference from the mean time of 28 seconds which is not to be accounted for by the small variation of current density due to change in the surface of the wire exposed. A large number of similar determinations were made, using current densities ranging from 15 to 80 milliamperes with a corresponding time required to passivify the iron varying from 21 minutes to 3 seconds. All experiments showed a similar lack of agreement between individual measurements. Sets of determination were also made at 18° and at 25°, using the cells in a thermostat. These gave even less satisfactory results, due, in part, to the greater loss of iron while rendering the anode passive, greater current densities being needed at higher temperatures. These extended experiments failed to show the desired uniformity of relation between two variables and the suspicion that all the factors influencing the passive condition were not yet at hand grew more pronounced.

II. DISSOLVED OXYGEN AS RELATED TO PASSIVITY.

During the progress of the work it was noted that minute bubbles of oxygen occasionally adhered to the surface of the iron even after it became wholly active and that in such cases the metal became passive more readily. Jarring the electrode, or stirring the electrolyte, partially obviated this difficulty, but when minute bubbles were allowed to persist, the results varied widely. This suggested that *dissolved* oxygen in the neighborhood of the electrode might be a factor in the problem.

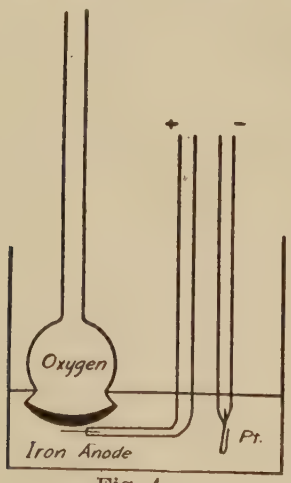

Fig. 4.

To test the question an apparatus, Fig. 4, was so arranged that the iron anode could be held close beneath an atmosphere of oxygen which was kept at constant pressure in the thistle tube. By rotating the tube bearing the anode, it could be readily removed somewhat distant from this sustained concentration of oxygen. The results obtained (Table VI) indicate clearly that iron is much more readily made passive near the oxygen surface. When hydrogen gas or nitrogen was substituted for oxygen no such effect was produced.

TABLE VI.

N/5 H_2SO_4; room temperature; 5 mm. iron wire exposed.

No.	Time in sec. for 30 m. amps. to passivify.	Diam. of wire in mm.	Relation of iron to oxygen bubbles.	No.	Time in sec. for 30 m. amps. to passivify.	Diam. of wire in mm.	Relation of iron to oxygen bubbles.
1.....	10	0.710	Under	12.....	20	0.702	Under
2.....	11	0.709	Under	13.....	37	0.700	Not under
3.....	16	0.708	Under	14.....	17	0.700	Under
4.....	17	0.708	Under	15.....	23	0.700	Under
5.....	13	0.708	Under	16.....	24	0.697	Under
6.....	13	0.707	Under	17.....	45	0.693	Not under
7.....	27	0.706	Not under	18.....	19	0.693	Under
8.....	26	0.706	Not under	19.....	47	0.692	Not under
9.....	15	0.705	Under	20.....	25	0.688	Under
10.....	22	0.705	Under	21.....	63	0.688	Not under
11.....	22	0.704	Under	22.....	30	0.680	Under

Nos. 3-6 show an average a little above 15 seconds.

Nos. 7 and 8 not under the oxygen required about twice the time.

No. 9 under the oxygen, goes down to 15 seconds again.

After No. 9, the iron was removed from the electrolyte, washed and dried and the experiment discontinued for about 20-25 minutes and after this more time was required to render the iron passive but in general the time required under the oxygen was about half that required when not directly under the bubble of oxygen.

The higher concentrations of oxygen were next investigated with the apparatus arranged as in Fig. 5. A tank of oxygen was connected to a manometer and thence to the cell, which was closed by a rubber stopper held in place by a pressure clamp. The anode and cathode were arranged as before, except that the anode was held in place by Khotenski's wax and then coated with paraffin. A length of 5 mm. was exposed. The electrical connections were as before. The cell was placed in an ice bath not shown in the cut. All factors shown to influence to passivity were thus held constant except the concentration of the oxygen above, and consequently in the solution. After a desired oxygen pressure had been established and sufficient time to secure saturation had elapsed, the cell was shaken with a circular motion to insure freedom from anode bubbles. After thirty seconds the circuit was closed and the time required for a current of 15 milliamperes to passivify the iron was measured. The circuit was

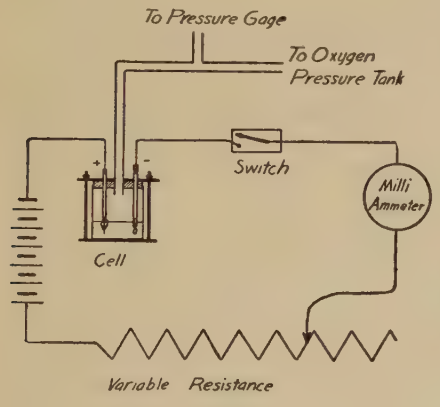

Fig. 5.

TABLE VII.

No.	Time in seconds to passivify the iron.	Oxygen pressure lbs. per sq. in.
1.....	?	air that is oxygen, 3 lbs.
2.....	40	
3.....	45	
4.....	45	
5.....	45	
6.....	20	
7.....	21	
8.....	22	15 lbs.
9.....	20	
10.....	20	
11.....	12	
12.....	11	
13.....	12	
14.....	10½	51 lbs.
15.....	11	
16.....	11	
17.....	11	
18.....	7	
19.....	6½	
20.....	7	57.4 lbs.
21.....	6½	
22.....	7	
23.....	5	
24.....	6	
25.....	5	65.88 lbs.
26.....	5	
27.....	4	
28.....	4½	
29.....	5	81.34 lbs.
30.....	4	
31.....	4	
32.....	34	Here fresh electrolyte substituted. Saturated with air, i. e., oxygen, 3 lbs.
33.....	45	
34.....	45	

0.2 N sulfuric acid. 5 mm. length of iron wire exposed. Initial diameter 0.710 mm. Final diameter 0.680 mm. 15 ma. current employed while rendering iron passive.

then opened and measurements repeated. Table VII shows a series for pressures of oxygen ranging from 3 lbs. per sq. in. to 81 lbs. with one section of wire. The values so obtained represent a very satisfactory constancy and are typical of a large number of series which are not detailed.

It will be observed that loss of surface area, due to solution of the iron, is not a seriously disturbing factor since the decrease of diameter of the iron in successive determinations is about 0.0009 mm., and only 0.03 mm., in the whole series of 34 determinations. When an oxygen pressure of 0.2 atmosphere, secured by air pressure was used no such uniform agreement in time, required to render iron passive, could be obtained. This accounts fully for the long-continued failure to secure quantitative results under atmospheric pressures.

Similar experiments were conducted using 0.2 N sulfuric acid, which had been boiled to expel dissolved gases, and with the cell connected to a suction pump. The results obtained showed great irregularity, but the time required to render passive was much longer than under ordinary conditions.

When 0.2 nitric acid was used as the electrolyte, conditions be-

ing otherwise the same as those above detailed, the results were different; the iron becomes active much less readily in nitric acid. It was finally found necessary to remove the iron after each determination, wash with 0.2 N sulfuric acid and with water before a satisfactory repetition could be obtained. With nitric acid also, the factor of long continued passage of the current is less marked in its effect than with sulfuric acid, and a critical density is more apparent. Below this critical density, even long continued passage of the current only infrequently produced passivity. If the current density was sufficiently great, passivity was established practically instantly. For 0.2 N nitric acid solution at atmospheric pressure, i. e., about 3 lbs. per sq. in. of oxygen pressure, the critical current was found to be 20 milliamperes. At 56 lbs. oxygen pressure, the critical current was 13 milliamperes. It will be observed that increase of oxygen pressure here lowers the current density required to render the iron passive.

In 0.01 N hydrochloric acid with 53 lbs. oxygen pressure, oxygen was evolved freely and the other phenomena of passivity appeared when the current density was relatively high. When the other conditions, except the pressure of gas imposed, were similar, there was only a very slight evolution of gas at the anode. With 0.02 N hydrochloric acid less oxygen was evolved, and with 0.05 N and 0.1 N solutions no indications of passivity either with or without oxygen pressure could be observed. It appears that with a sufficient dilution of chlorine ions the passive state can be induced in halogen solutions: a fact not heretofore demonstrated.

From the foregoing results it appears that to the five factors mentioned in the introduction, which condition the passive state, are to be added two others: The character and extent of motion of the electrolyte and the concentration of dissolved oxygen about the anode. When all of these factors are being taken into account, constant results are obtainable with respect to the time required to render iron passive with a given current in sulfuric acid, and in nitric acid a critical current density is determinable.

III. THE BEARING OF ELECTRODE POTENTIAL ON PASSIVITY.

The discovery that the concentration of oxygen dissolved in the electrolyte was a factor influencing the anodic passivity of iron raised a question as to its possible effect on the electrode potential of iron. It has been assumed by Fredenhagen, Muthman, Fradenberger and others that the anodic potential is a measure of the passivification.

In attempting to answer these questions results were obtained which were not so directly related to passivity as was expected when the measurements were undertaken, however, they were of such interest as to deserve a detailed report.

The whole situation of electrode potentials is far from being in a satisfactory condition, and due to its importance and interest should prove a fruitful field for a thorough and systematic experimental development. Approximate electromotive values are given by most authors; while for iron, as Heathcote[3] has pointed out, the values given by the different authorities show a surprising lack of agreement. In most texts the potential value of 0.940 volts is given for iron in contact, at room temperature, with a solution containing one gram mole of iron ions per liter measured against a normal calomel electrode as zero. Since all of the studies on passivity, described in the first two parts of this report, were made with iron immersed in 0.2 N sulfuric acid and at the temperature of an ice bath, these conditions were adopted for use in these potential measurements. This was done so that the two phases of the work could be more readily compared.

In order to work with high gas pressures the normal calomel electrode was modified somewhat in form. The cell, (See Fig. 6) used was kindly constructed by Prof. Wm. M. Dehn and differed from the ordinary cell in the following particulars: the platinum contact with mercury was sealed in through the glass at the bottom of the cell; the tube for contact with the electrolyte bearing the metal under investigation was drawn out to a long and rather fine capillary; a dropping funnel, for introducing the normal potassium chloride, was sealed on the cell at the top. Thus it was possible to keep the cell always full of the normal potassium chloride solution, and this absence of an air space prevented external pressure from forcing any other electrolyte back into the body of the cell. The capillary tube prevented a rapid diffusion and consequent contamination. After each set of measurements fresh normal potassium chloride was introduced through the dropping funnel thus forcing that out in the capillary which had been in contact with the outside electrolyte.

That the value of this cell did not change, in the course of the six months that it was used, was shown by checking it from time to time with two normal calomel electrodes of the ordinary type and the values obtained for all three did not show any noticeable variation. Against amalgamated zinc, immersed in molor zinc sulphate and at room temperature, all gave values varying but little from 1.08 volts,

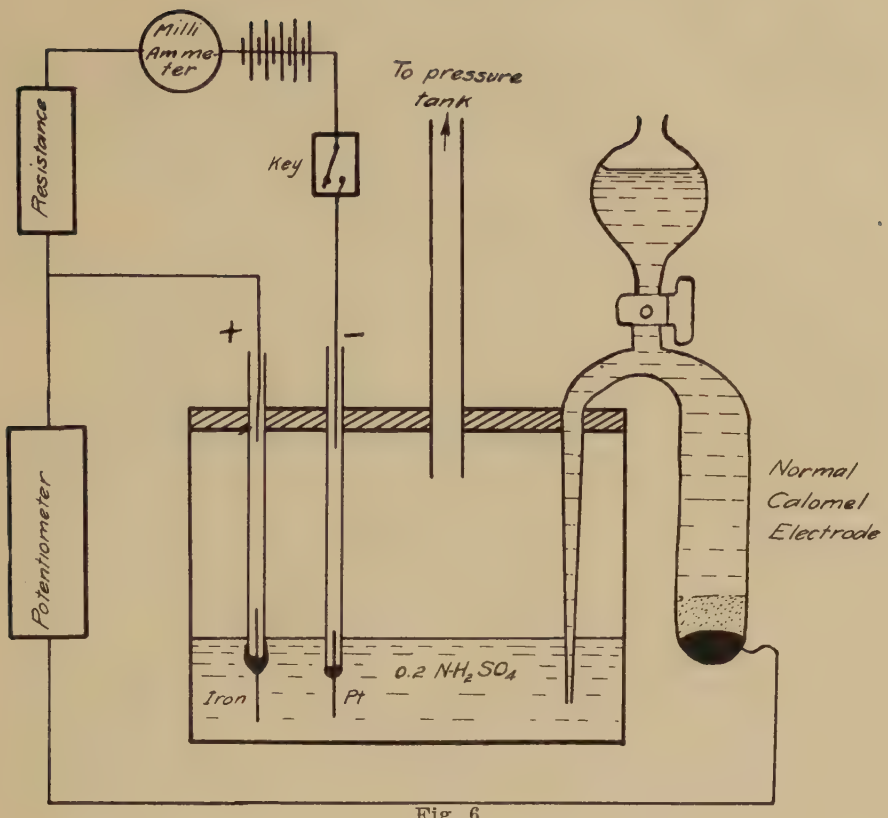

Fig. 6.

which is given as the characteristic potential difference of this combination. The potentials measured are compared with the normal calomel cell as zero and the negative sign indicates potentials differing from the calomel as do the noble metals.

A potentiometer, capable of detecting potential differences of one ten thousandth of a volt, was used, but readings were taken only to the third decimal, for the potential fluctuates from moment to moment due to a variety of causes such as local concentration and thermal effects. In numerous cases, even this degree of accuracy was not practical. The instrument used was very satisfactory as it allowed of quick and accurate adjustment. The initial electromotive force of different sections of wire immediately after immersion in the sulfuric acid was not always the same, but ranged between the limits +0.522 and +0.506 volts. The variation in the initial active potential is perhaps somewhat related to a similar variation in the differences of time required for a given current density to pas-

sivify different sections of wire. These small variations are probably to be ascribed to variations in character of the electrode material. As the iron stands in contact with the acid its potential gradually changes as shown in Table VIII, though the variations here are of

TABLE VIII.

Time in minutes		E. M. F. Volts
Start		+0.511
2		+0.513
19		+0.523
31		+0.524
37		+0.524
45		+0.527
60		+0.530
72		+0.536
87		+0.536
125		+0.539
140		+0.542
150		+0.544
	Iron changed to fresh electrolyte	
152		+0.549
153		+0.549
156		+0.550

a more uniform character and of greater magnitude than were shown in all cases. An exactly similar set of figures appear in Table IX, where at the end of seven minutes hydrogen gas, at 50 lbs. pressure

TABLE IX.

Time in minutes	E. M. F.	Hydrogen Pressure
Start	0.507	No external gas pressure
2	0.510	" " " "
4	0.511	" " " "
7	0.513	" " " "
10	0.515	Hydrogen pressure 50 lbs. per sq. in.
12	0.517	Pressure same
13	0.518	" "
15	0.518	" "
18	0.519	" "
20	0.520	" "
	Oxygen Pressure	
Start	0.510	No external pressure
4	0.514	" " "
7	0.515	" " "
8	0.517	Oxygen pressure 53 lbs. per sq. in.
9	0.519	Same pressure of Oxygen
13	0.521	" " " "
18	0.523	" " " "
19	0.524	" " " "
20	0.524	" " " "
25	0.526	" " " "
27	0.527	" " " "

per sq. in., was applied. As a comparison of Table VIII and IX will show, the gas at this pressure caused no noticeable deviation from the normal behavior. Oxygen pressure showed a corresponding lack of effect (See Table IX) on prolonged application, thus allowing the electrolyte to become saturated with the gas.

It may therefore be concluded that neither mechanical pressures nor the saturation of the electrolyte with hydrogen or oxygen produces an effect on the electromotive force of iron when immersed in 0.2 N sulfuric acid.

The second step was to obtain the electrode potential of iron electrodes held in the passive condition by a small current, and subsequently to determine the effect of oxygen and other gaseous pressures. The apparatus is shown in Fig. 6, and requires but little explanation. The iron electrode was in series with a platinum electrode, a milliammeter, five lead storage batteries, a variable resistance and a key. The potential difference between the normal calomel electrode and the iron electrode could be measured at any time by the potentiometer which was connected through a commutator.

With the arrangement just described, a section of wire was rendered passive at high current density and then the resistance of the external circuit increased until the polarizing current had dropped to 10 milliamperes. The first reading of the potential just after passivification were always higher than subsequent values. These changes, as appears in Table X, show that polarized passive electrode becomes

TABLE X.

Time in minutes	E. M. F.	
Start	+0.510	
4	+0.512	
7	—1.790	Iron passive, 10 M. A. flowing
10	—1.789	" " " " "
16	—1.785	" " " " "
20	—1.782	" " " " "
22	—1.783	" " " " "
24	—1.781	" " " " "

less noble on standing even though a small external current is maintained to sustain the polarization. This is exactly analagous to the behavior of the active iron when no external current is applied. (Compare Table VIII.)

The effect on this polarization potential produced by the application to the surface of the electrolyte, of oxygen gas under pressure is shown in Table XI, where it is clearly evident that coincident with

TABLE XI.

Time in minutes	E. M. F.	
Start	+0.506	No pressure, no external current
1	+0.560	" " " " "
2	+0.507	" " " " "
	Iron rendered passive and then current reduced to 10 M. A.	
3-5	?	10 M. A. current. Potential varying
7	—1.820	" " " "
10	—1.816	" " " "
12	—1.818	" " " "
15		" " " " Oxygen pressure 42 lbs. sq. in.
17	—1.806	" " " " " " " " " "
22	—1.807	" " " " " " " " " "
23		" " " " Pressure off
25	—1.811	" " " " " "
30	—1.788	" " " " Oxygen pressure 42 lbs. sq. in.
32	—1.786	" " " " " " " " " "
33	—1.788	" " " " " " " " " "
36	—1.796	" " " " " off
38	—1.798	" " " " " "
39	—1.796	" " " " " "
41	—1.796	" " " " " "
43		" " " " " pressure 48 lbs. sq. in.
44	—1.786	" " " " " " " " " "
46	—1.787	" " " " " " " " " "
48	—1.788	" " " " " " " " " "
53	—1.793	" " " " " " " " " "
54	+0.518	No external current or pressure

the rise in pressure there is a fall in potential, and that with the release of the pressure the potential again rises, but not as high as it was when the pressure was first applied. This is not surprising in view of the fact just established in the previous experiment, that for an anodically polarized passive iron electrode the value of its potential gradually decreased with time.

That the change in potential is due to the mechanical pressure and is independent of the nature of the gas is also made clear by the data in Table XII. A range of oxygen pressures was used and then a corresponding treatment using hydrogen pressure. The results as shown here are more uniform than those exhibited by most electrodes. The measurements in the table were all made on one section of iron wire but the data indicated was previously ascertained on divers sections and the results as shown are typical and are confirmed by numerous independent tests. The table shows the most complete and satisfactory single series of measurements.

When this work was undertaken it was expected that if the gas pressure produced any effect it would be after the electrolyte had become saturated with the gas, and that if the hydogen produced any result at all that it would be opposite to that caused by oxygen. The

TABLE XII.

Time in minutes	E. M. F.	
Start	+0.510	
3	+0.510	Iron active and no external current
5	+0.510	
8	—1.784	Iron rendered passive then current lowered to 10 M.A.
12	—1.771	
13	—1.771	Lowered to 10 M. A.
14	—1.730	Oxygen pressure turned on 43.9 lbs.
15	—1.768	Oxygen pressure off
17	—1.771	Oxygen pressure 18.7 lbs.
18	—1.730	" " 43.9 "
19	—1.730	" " 43.9 "
20	—1.730	" " 43.9 "
21	—1.768	No pressure
23	—1.730	Oxygen pressure 43.9 lbs.
25	—1.748	" " 30.5 "
26	—1.760	" " 25.8 "
27	—1.770	No pressure
28	—1.760	Oxygen pressure 25.8 lbs.
30	—1.751	" " 30.5 "
31	—1.740	" " 34.6 "
32	—1.730	" " 43.9 "
34	—1.767	No pressure
35	+0.520	External 10 M. A. current stopped
38	+0.520	Iron active
40	—1.775	Iron rendered passive and current lowered to 10 M. A.
41	—1.776	
44	—1.728	Hydrogen pressure 43.9 lbs.
48	—1.747	" " 34 "
50	—1.755	" " 30.5 "
51	—1.761	" " 25.8 "
53	—1.770	No pressure

fact that the change of potential was coincident with the application of the pressure and independent of the gas led to the suspicion that perhaps the phenomena was not characteristic of passive iron alone. To test this potential determinations were made, under analagous conditions, on the following electrodes; an iron cathode, platinum anode and cathode, and a copper anode Table XIII shows the changes produced. The data for cathodes is only approximate, due to lack of constancy, so that the results are only qualitative although the change with pressure is quite evident and it becomes clear that *on application of gaseous pressure anodes, from which gas is being evolved, become more positive and cathodes more negative.* Nernst's equation for the potential of metal electrodes can be extended over to the effects just described if the anode is considered as coated with an oxygen film or charged with oxygen, as by occlusion. In the equation $E = \frac{RT}{F\,n}\left\{\text{nat log } \frac{P}{p}\right\}$, P would represent the solution tension of the oxygen which is associated with the metal and p would represent the

TABLE XIII.

Platinum Anode and Gas Pressure.

N/5 H_2SO_4; temperature 0° C. Polarizing Current 8 M. A.

Time in minutes	E. M. F.	Hydrogen pressure lbs. per sq. in.
Start	—1.899	0
1	—1.898	0
2	—1.879	50
3	—1.882	40
7	—1.884	38
9	—1.885	35
12	—1.890	28
13	—1.898	0
15	—1.898	28
18	—1.893	34
21	—1.886	46
24	—1.882	57
26	—1.882	57
27	—1.903	0

Iron Cathode and Gas Pressure

Time in minutes	E. M. F.	Pressure
Start	+0.069	No pressure
4	+1.069	" "
7	+1.058	Hydrogen 40 lbs. per sq. in.
9	+1.057	" " " "
10	+1.057	" " " "
15	+1.065	No pressure
20	+1.069	" "

Copper Cathode and Gas Pressure

Time in minutes	E. M. F.	Pressure
Start	+1.141	No pressure
2	+1.140	" "
4	+1.127	Oxygen pressure 29 lbs. per sq. in.
6	+1.050	41 lbs. per sq. in.
7	+1.160	Pressure off.

Platinum Cathode and Gas Pressure

Time in minutes	E. M. F.	Pressure
Start	+1.680	No pressure
2	+0.680	" "
5	+0.685	" "
7	+0.673	Oxygen pressure 43 lbs. per sq. in.
8	+0.697	No pressure
10	+0.673	Oxygen pressure 43 lbs. per sq. in.
11	+0.676	" " " " " "
13	+0.793	No pressure

osmotic pressure of oxygen ions in the solution. The application of any external pressure would then, immediately increase the concentration of the oxygen associated with the metal and thus raise the solution tension P and the value of E the potential. On the other hand,

the increase of the value of the osmotic pressure p would be a slow process so that on application of external pressure the value P increases faster than p and there results the rise in anode potential. Exactly analogous relation exist in the case of the cathode and a similar explanation of the increased negativity of cathodes can be made. From the form of the factor (nat log P/p) it is to be expected that the change of potential with pressures, such as those used, would be small and taking into consideration the facts indicating the presence of an oxygen film this is the most useful hypothesis to apply in this case where the change in potential is small, such as would be expected if a gas film were considered, while if occluded oxygen or an oxygen charge is assumed we are at a loss due to lack of knowledge of the coefficient of occlusion. The effects of pressure on potential as above detailed are new and merit fuller investigation. The potential measurements led directly to the studies which follow.

In the hope of obtaining a more intimate knowledge of the processes of passivification a study was made of the changes in the potential of iron while it was passing from the active to the passive state, and the reverse. The conditions and apparatus used were exactly the same as in the work just detailed. The field of polarization potentials is one of unusual difficulty because an electrode in contact with an electrolyte shows great variation in behavior, especially when an external current is impressed. Using the potentiometer previously described the changes in potential when the iron was used as an anode were found to be interesting, but when attempts were made to get accurate readings of the momentary values it was found that satisfactory and reproducible values could not be obtained. For the sake of clearness the observed behavior will be described and then an account will be given of the method used in obtaining the results. The potential behavior of iron in contact with fifth normal sulphuric acid when no external current is flowing has been previously described, and as was shown in Table VIII, the potential gradually became more positive on standing. This value does not attain constancy in the course of two hours. Different specimens of iron wire on immersion in the acid show potentials ranging from +0.506 to +0.522 volts. When the external current, 10 m. amps., was applied the potential quickly became less positive and by the close of two seconds it had generally passed through the value +0.11 volts (See Fig. 7). Then the change became slower and there was a continuous fall to about —0.15, and this was soon followed by a very rapid fall to the neighborhood of —1.85. Coincident with this last sudden drop the iron became passive and

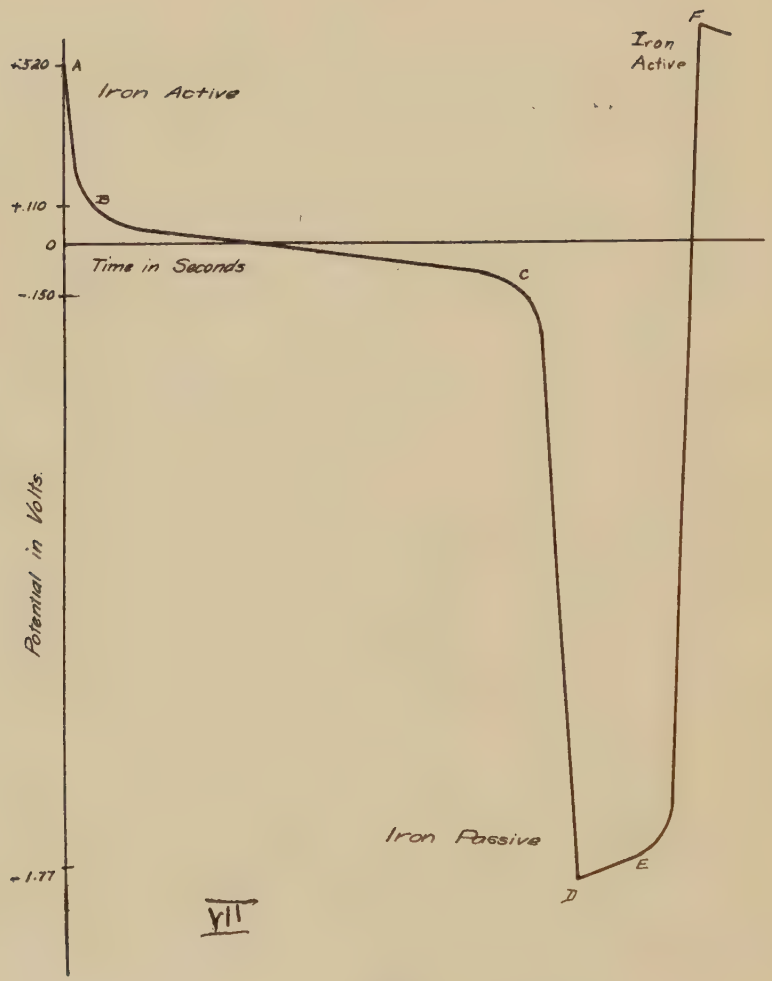

Fig. 7.

the resistance at the anode surface increased as was shown by the fall in polarizing current.

When the external current was stopped the potential did not change greatly for a little while and then there was a very sudden rise as the iron became active. The wait before activification sets in is longer when the passive electrode has been polarized for a greater length of time or when a high current has been used. On becoming active, with no external current flowing, the potential usually rose to a value slightly above 0.6 volts, which is higher than the initial value on first immersing the iron in the electrolyte. Potentiometer readings

could not be made in the ordinary way since during the processes, the values were constantly changing. The current through the external circuit was changing in an analagous manner and this tends to show that the change of potential is associated with a change in resistance at the electrode surface. The external resistance was so arranged that there was, as nearly as possible a current of 10 milli-amperes flowing during the period shown on the curve by the length B to C. Using these conditions the method adopted was to choose a time, say five seconds, after the external current was applied and then attempt to get as good readings of the potential at this time as possible. The potentiometer circuit was closed with the instrument set at the estimated potential, then by the vigor and direction of the galvanometer throw the setting was guessed and after the iron had been rendered active again another trial was made at the end of the fifth second. Thus a value was approached, but there was always the difficulty that the potential of any particular specimen of wire was always changing and different samples gave different values so that the exact quantitative results were impossible. However, the graph gives a very good idea of the trend of events and the failure to obtain concordant results is characteristic of work in this field. Heathcote[3] attempted a similar set with even less success although he arrived at a similar curve for the changes of potential as iron becomes passive. The form of the curve (See Fig. 7) is such that it presents rather strong evidence in favor of the idea that the establishment of passivity is the result of two processes. The first of these would consist of the formation of a layer of insoluble material such as ferrous oxide. This would not be, of necessity, a firmly adherent coating and might be pierced by holes or pores. Its initial formation would correspond to the part of the curve from A to B. The other process would be the establishment of a film of oxygen gas which would form a complete cover over the electrode. The transition between these two processes is represented by the slow drop in potential shown between B and C, after which the cover rapidly becomes complete and potential drops from C to D. In a similar way the curve indicating that activification is a single process or at best prac-

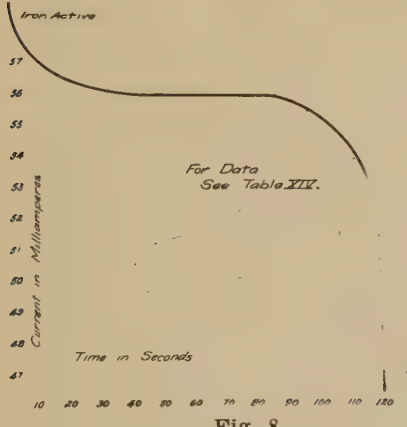

Fig. 8.

tically the simultaneous removal of both the oxygen and the oxide coats. This removal is exceptionally complete as is shown by the final maximum potential. This may also be due to the removal of the occluded gases.

That the variation of anode potential is associated with a change of resistance at the anode surface is confirmed by the change in the polarizing current as the iron becomes passive. The graph, (See Fig. 8) shows that the variation in external current with time is exactly analagous to the changes in the anode potential during the process of passivification. In taking the date (Table XIV) a longer section of

TABLE XIV.

Time in seconds	Current, Milli. Amps.	Conditions
0	59	
3	58	Temperature 18° C.
10	57	0.2 N H_2SO_4
17	56½	
32	56¼	Diameter of iron wire 0.770 mm.
75	56	25 mm. wire exposed.
85	56	The wire had previously been
95	55½	rendered passive two or three times.
105	55	Several successive determinations
110	54	on the same section of wire gave
117	53	exactly similar results. Through-
120	46½	out the work the external resistance was not changed.

iron was used in order to obtain figures of greater magnitude. The bearing of these curves on the explanation of passivity will be given in the theoretical discussion at the close of the paper. As a preliminary some of the facts that are considered of critical importance will be given, followed by a review of the theories that are now exerting the greatest influence. Since the historical development has been well treated in the literature a number of times, space will be used here simply to present the facts and theories.

The isolated facts of passivity are so numerous and so varied that for the purpose of this discussion it will be sufficient to mention only a few of the more important and those which bear most directly on the theoretical considerations that will follow. The summaries by Byers[2] and by Heathcote[3] as well as the Faraday Society Symposium[15] to which reference has been previously made, were freely consulted and due credit is given to these reviews where the facts are more completely detailed and the various authors and references are given.

The discovery of passivity is accredited to James Keir[1], who in 1790 investigated the observation of Bergman[16] that some samples

of iron will displace silver from its salts while others will not. As an introduction to the phenomena of passivity a quotation of Keir's report of one of his most important observations will be valuable. He states, "I digested a piece of fine silver wire in pure and pale nitrous (nitric) acid, and while the solution was going on and before saturation was completed I poured a portion of the solution upon pieces of clean and newly scraped iron wire into a wine glass and observed a sudden and copious precipitation of silver. The precipitate was at first black, then it assumed the appearance of silver and was five to six times larger in diameter than the piece of iron wire it enveloped. The action of the acid on the iron continued some little time and then ceased, the silver redissolved, the liquor became clear, and the iron remained bright and undisturbed in the bottom of the wine glass, where it continued during several weeks without suffering any change or effecting any precipitation of the silver."

He noted that the passive iron became active on being scratched or jarred or on contact with a piece of active iron. Indeed he reported that if a piece of passive iron was placed close to, but not touching, a sample of passive iron which lay in an acid solution the passive iron became active. The next important contribution after the original work of Keir was that of Schönbein[17] who showed that iron could be rendered passive by using it an anode immersed in water solutions of oxygen acids. The investigations of Hittorf which came about sixty years later are extremely interesting since he found that "active" chromium dissolves in the divalent form while "passive" chromium dissolves at a much higher potential with the formation of compounds in which chromium has the valence of six. Periodic passivity deserves special mention as it shows very clearly that, in some instances at least, the active and passive states can be in a very delicate equilibrium with respect to each other, for under the right conditions a piece of iron lying in nitric acid will show alternate periods of activity and passivity. There does not seem to be any regularity to these pulsations but on the contrary the iron may lie for a considerable time and then suddenly manifest activity almost with explosive violence or, on the other hand, the change may start at some particular point and spread gradually over the whole surface. There does not seem to be any real passivity in the sense that the metal is completely inert for in all cases there is some loss due to solution. This, however, is not surprising for even platinum dissolves slightly in contact with electrolytes and under the right conditions it dissolves with vigor as shown by Ruer[18] who finds that when he subjects a plat-

inum pole to an alternating current and makes it simultaneously the anode of a direct current with small current density, the platinum dissolves extensively. The same results were obtained when instead of using the direct current an oxidizing agent was placed in the electrolyte. The experimental work on passivity has been very extended and it appears that most of the metals exhibit phenomena which can be classed under this head. In some cases a visible protecting coating of oxides or some other insoluble material forms, while at other times surface coatings have not been demonstrated by very refined measurements of the reflecting power of the surfaces[19]. On the other hand there is some evidence that passive anodes show capacity effects which are accounted for on the basis of a film of oxide or oxygen. Other facts will be included in the discussion of the theories which follows:

THE FARADAY DELICATE EQUILIBRIUM HYPOTHESIS.

Schönbein the discoverer of anodic passivity did not at first offer a theory to account for the inactive condition of iron but wrote Faraday asking for an explanation. Faraday[20] replied saying: "My strong impression is that the iron is oxidized, or the superficial particles of the metal are in such relation to the oxygen of the electrolyte as to be equivalent to an oxidation." He gave as reasons in favor of his theory, that all known passivity phenomena were oxidation processes, that iron coated with oxide is insoluble in acids, and that the passive condition disappears on polishing the metal. Schönbein opposed this view and produced evidence which did not accord well with it and Faraday modified his statement to the extent that he no longer maintained that the coating consisted of one of the known oxides, but resembled more *a condition of delicate equilibrium.* Attention is called to this last clause, for Faraday is generally credited with the oxide film theory but as this clearly shows, he realized that the situation was one of dynamic equilibrium.

THE OXIDE THEORY.

While this theory is clearly a survival of Faraday's original idea it has seemed desirable to class it under a separate head. There is no lack of instances where an anodic solution certain metals become coated with an adhering film of oxide or other insoluble material. E. Muller and Spitzer[21] showed that cobalt, iron and nickel on anodic polarization in alkali become coated with oxide and simultaneously became passive. Haber and Mitland[22] showed that in contrast to the

behavior of alkali of moderate concentration very strong alkali renders iron active and that it acts by first dissolving a superficial coat of oxide formed when the iron became passive. Senter[15] in his discussion before the Faraday Society (1914) points out that "the weak point of such investigation is that they are carried out in alkaline or neutral solutions, and therefore cannot afford an explanation of passivity in general, especially in acid solutions." It is perhaps fitting at this point to raise the question as to whether there is any explanation of passivity in general, or whether, in particular cases the actual mechanism of passivity depends upon the conditions. This idea will be developed in more detail later. Manchot[23] is one of the most recent supporters of the oxide theory. His evidence is based on the fact that silver, iron, copper, cadmium, zinc or lead, plates which have been polished do not react with ozone but after anodic polarization in NaOH they do react with ozone thus proving that an oxide film has been formed although none is visible. That passivity disappears on standing he attributes to a change in the surface of the oxide by which it ceases to be a continuous film and contracts to granular particles thus exposing the free metal again.

THE VALENCY THEORY OF PASSIVITY.

This theory has had little support although it is particularly in accord with the behavior of chromium and molybdenum, which when passive dissolves with higher valency than when active. However, it has not been shown that the solution of these metals in a higher state of oxidation when passive is not due to a secondary reaction. The theory is based on Kruger's[25] assumption that the modifications of a metal with different valencies are all present in the solid metal in proportions depending on the conditions, as temperature, etc. This theory of Kruger and Finkelstein then accounts for passivity on the actual condition of the metal itself. While interesting it has not been productive although attention should be called here to the fact that chromium becomes passive in halogen solutions. The most recent work along this line is that of W. J. Muller, 1910[24] who finds that in KOH solutions thallium goes into solution with valency varying from one to three.

THE OXYGEN CHARGE HYPOTHESIS.

Fredenhagen[26], who first suggested this hypothesis, considered that anodic oxygen depresses the velocity of the reaction of the metal with itself to such an extent that the anode covers itself completely

with a film of oxygen or an alloy of oxygen and the metal, thus inducing passivity. Considering first the idea of an oxygen film envelope covering and protecting the metal surface, this view taken in the extreme, would mean, just as the oxide film, that there is a two phase system. On the other hand, the idea of an oxygen alloy involves a one phase system of continuously variable composition, and a correspondingly variable electrolytic solution pressure. In addition it may be stated that it is quite plausible that should they exist either one or both of the above systems might be complicated by the formation of an oxide, which would exist in equilibrium. Such a state of affairs would remind one of Faraday's view that the condition is one of "very delicate equilibrium."

HYDROGEN ACTIVIFICATION HYPOTHESIS.

That all metals in the pure condition are passive is suggested by Foerster[27], and that they become active under the influence of catalytic agents. Hydrogen is suggested as the most important of these catalysts. E. Grave[28] disagrees with him to the extent of saying that hydrogen *ions* are the activating agents. Heating metals in nitrogen, vacuum, etc., and then testing the passivity has not yet settled the question since different investigators obtain results which do not agree. Of course it is probably not true that heating will completely free the metals from dissolved gases, and this in indicated by the fact that cathodic bombardment of iron will cause gas to be evolved for an indefinite period of time. The work of Grave above referred to has shown strong evidence that a metal can be rendered active by the diffusion of hydrogen ions. On the whole it has been fairly well established that gases may play an important part as catalysts; yet our scanty knowledge of absorption or occlusion of gases by metals limit interpretation of results. The difficulties encountered shows that we very rarely work with absolutely pure materials and, since catalyzers are effective even though they may be present in the merest traces, our system may be complicated by unknown factors. It is most certainly true that different samples of iron show a marked difference of behavior.

The details of the hydrogen activification hypothesis as worked out by Grave[15] are not as illuminating as one might hope. He says, "that just as water and other liquids do not boil even when their vapor pressure is equal to the superincumbent pressure, unless a catalyst, such as air is present, so metals which can be passified dissolve rapidly only in the pressure of a catalyst. It might be supposed that hydrogen,

like air in boiling, forms a nucleus around which the metal ions might collect."

PRIMARY ANODIC DISCHARGE HYPOTHESIS.

Sackur[29] suggests that the solution of a metal as an anode is not due to the passage of ions of the metal into the solution but rather to the primary discharge of the ions which then react directly with the metal itself. On the basis of this idea he gave a rather complicated explanation which has not proved useful; but the idea of primary anodic discharge is one that promises to play an important part in future passivity considerations, as well as to find a place in the other fields of electro-chemistry.

THE ION HYDRATION HYPOTHESIS OF LE BLANC.

Le Blanc[30] was the first to put forward the idea that the passive state is due to a change in the velocity of ionization. How this change was brought about he did not at first attempt to say. He has now extended his views and accounts for the retardation on the basis of hydration of the ions. He says the idea that ions of the metal are not formed primarily may be justified, but he contends that this assumption is not necessary. He prefers to think that the ions of the metal are primarily formed and practically with infinite velocity but that they tend to become hydrated at the surface of the electrode. The magnitude of the potential difference between the metal and the electrolyte would then depend upon the concentration of the non-hydrated, free ions, and this latter again upon the velocity of hydration. He is thus able to account for anodic and cathodic polarization. With passive metals ionic hydration occurs so slowly at the anode that the concentration of free ions, and therefore the potential difference, becomes so great that visible separation of the negative radical or of oxygen results.

The above is not a complete catalogue of the hypotheses that have been offered for passivity, but the most productive in stimulating research. No one of them will completely correlate and explain all of the wide range of facts bearing on the question. Each has its advantages as well as its limitations.

In view of the diversity of opinion and wide range it seems, as already suggested, that there is no one general explanation of passivity but rather that in each individual case the loss of activity is dependent upon the conditions, and that the explanation of the mechanism of the reaction will not come at one step by the announce-

ment of an all embracing hypothesis but that each individual case must be worked out independently. Iron anodes in sulphuric acid behave differently depending upon the circumstances. This has been pointed out by Schulze[15] who says that "in dilute sulphuric acid iron shows passivity; in concentrated acid, valve action; in intermediate concentration an unstable valve action succeeded by passivity." The nature of valve action is made clear by the behavior of aluminium, when used as an anode in a suitable electrolyte a film of aluminium oxide is formed and oxygen is evolved. The film is at first so thin that it is invisible but gradually builds up to a light gray coating pierced by very numerous holes of microscopic size. This film absorbs about 5% of the current, the rest being used in the formation of the oxygen which escapes. The work and conclusion of Schulze, although bearing largely on valve action, throw interesting and valuable light on the passivity problem. The objection is often raised that, as in the case of iron, it is difficult to understand how oxides or hydroxides can exist in the presence of an acid electrolyte. Let us consider the case of a metal used as an anode when it is readily seen that there is no objection to the assumption that the surface of the metal is in contact with a neutral or alkaline medium, for since the anode is positively charged the hydrogen ions which bear a charge of like sign would be repelled, and their concentration materially reduced in the zone of contact between the electrolyte and anode. On the other hand negative ions would be attracted and increase the possibility of primary anionic discharge. Thus the relations of iron to sulphuric acid are very complex, and it will be sufficient to outline the conclusions arrived at with respect to the mechanism of the establishment of passivity in iron when used as an anode in fifth normal sulphuric acid, and under the *specific conditions* which have been maintained throughout the experimental work. There is little doubt but that we are concerned with surface conditions in our study of passivity. The potential curve shows that what occurs when passivity is established is a two process change. The external current curve agrees with this and indicates that after the application of the current there is almost at once an increase in the resistance at the surface of the electrode and that after a time there is another sudden and greater increase in this resistance.

Let us now consider a reaction mechanism that would account for these changes. The ordinary facts of electrode potentials show that metals can and do form ions directly so that even with our iron anode it is very probable that there is in equilibrium between the metal and its ions Fe metal (Fe^{++}). There is also evidence that the

anions may be attracted to the surface of the anode and discharge directly on the iron to form free (SO_4) radicals. These latter may react directly with the metal to form ferrous sulphate or may react with water to form oxygen atoms, $(SO_4) + H_2O = H_2SO_4 + (O)$. The oxygen atoms will react with the iron to form insoluble ferrous oxide $Fe + (O) = FeO$, or form molecular oxygen with the corresponding equilibria: $(O) + (O) = O_2$ in solution $=$ gas O_2. The principal equilibrium conditions are graphically illustrated in Fig. 9.

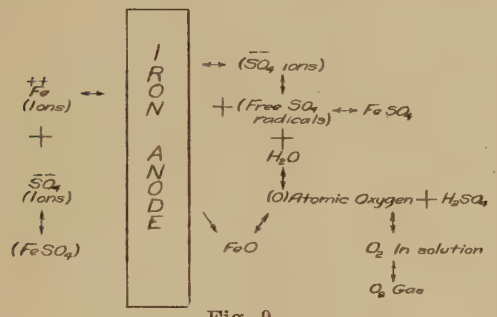

Fig. 9.

At the moment that the iron becomes an anode the most of the current is carried by means of iron ions entering the solution. But some anions are discharged directly on the surface of the iron and thus carry part of the current. These discharged ions can react with the iron to form ferrous sulphate, or with the water to form atomic oxygen which in turn can form ferrous oxide or oxygen molecules. In the latter case the solution would become saturated with oxygen and the gas would escape. But the formation of bubbles against an external pressure is a process that requires energy and it seems that so long as the free iron is readily available it requires less work to form the very insoluble ferrous oxide. However, the more ferrous oxide that is formed the less free iron is available and the more sulphate ions are primarily discharged so that the concentration of oxygen atoms would be so increased that the equilibrium would be changed to the direction of the formation of oxygen gas. On saturation, if the intensity of the reaction is sufficient, gas will form and the electrode become covered with a film of oxygen, the high resistance of which accounts for the last final drop in the potential and current curves. Due to the surface tension this formation of the gas film will be quick and complete.

This hypothesis fits the facts which are characteristic of the behavior of passive iron anodes under the conditions studied. Particular attention is called to the strong confirmatory evidence given by the fact, established in this research, *that dissolved oxygen increases the speed with which passivity is established.* (See Table VII.) With the high oxygen pressures the equilibrium conditions are made more favorable for the formation of the ferrous oxide and for the formation

of the oxide film. This is shown by a glance at the graphical representation given above. The fact that stirring retards the establishment of passivity is in perfect accord for it certainly would tend to tear off the film of oxide thus keeping fresh iron constantly exposed. However, after the passivity has been once established the tendency of stirring to destroy the condition would be reduced to a minimum by the influence of surface tension to keep the gas film intact. The reestablishment of activity occurs when, after the external current has been stopped, the gas film becomes ruptured in any way. Then the iron and oxide layer are in relation to each other very much like that of a short circuited cell and the activification occurs almost at once.

The retarding influence of higher temperatures offers no difficulty. The fact that very low current densities do not passivify is not surprising in view of the equilibrium conditions which have to be established. It is not my purpose to review all of the facts with the idea of showing how they accord with the explanation offered here.

SUMMARY.

The previously described retardation of the establishment of anodic passivity by the magnetic field was shown to be due to a stirring produced in the electrolyte when the cell was in the magnetic field. Exactly analogous retardations were produced by rotating the anode and the effect being greater with greater agitation. It was shown that the concentration of dissolved oxygen in the electrolyte has a very great influence in the direction of hastening the processes of establishing anodic passivity.

Interesting results on the relation of polarization potentials to external pressure were shown.

The curves showing the variation with time of electrode potential and of polarizing current, during the course of passivification, indicate that the two processes are involved.

A summary of the facts and theories of passivity is given and it is suggested that there is no general explanation of passivity, but that development must come through an understanding of the mechanism of individual cases. However, Faraday approached an explanation when he said that passivity is a condition of very delicate equilibrium.

A hypothetical explanation is given for the particular case studied.

As a final word the author wishes to express his great indebtedness to Professor Horace G. Byers for sustained inspiration, suggestion and counsel throughout the course of this research. Gratitude is expressed to Dr. Harlan L. Trumbull for helpful advice, and to Professor Henry L. Brakel for the use of apparatus from his electrical laboratory.

REFERENCES.

1 James Keir, Phil. Trans., **80**, 359, (1790).
2 Byers, Am. Chem. Soc., **30**, 1718, (1908).
3 Heathcote, J. Soc. Chem. Ind., 26, 899, (1907).
4 Byers & Darrin, J. Am. Chem. Soc., 32, 750, (1910).
5 Byers & Morgan, J. Am. Soc., 35, 1757, (1911).
6 Byers & Langdon, J. Am. Chem. Soc., 35, 759, (1913).
7 Fredenhagen, Z. physik. Chem., 43, 1; 63, 1.
8 Graves, Z. physik Chem., 77, 513.
9 Hurnuzecum, Elect. Rev., 42, 322.
10 Ashcroft, Electrochem. Met. Rev., 4, 145.
11 Frary, J. Am. Chem. Soc., 29, 1592.
12 Drude, Z. Electrochem, 8, 65; 8, 229; 9, 666.
13 Urbasch, Z. Electrochem, 7, 114; 7, 527.
14 Nichols & Franklin, Am. J. Sci., (3) **31**, 272, (1886); (3) **34**, 419, (1887).
15 "The Passivity of Metals," Reprint from the Trans. of the Faraday Society, 1914.
16 Bergman, Dissertat, divers phlogist. quant. metals.
17 Schonbein. Phil. Mag. 9, 53 (1836) Pogg. Ann., 37, 390, 590; 38, 444, 492, (1836); 137, 342, 351; 43, 1, (1838); 13, 103, 40, 193, 621; 41, 55; 59, 149.
18 Ruer, Zeit. Elek. Chem., 11, 661; 14, 309; 14, 663; 14, 679; also Z. Physik. Chem. 44, 97.
19 Muller & Koenigsberger, Zeit. Elektrochem., **13**, 659, (1907).
20 Faraday's "Experimental Researches."
21 Muller & Spitzer, Zeit. Anorg. Chem., 50, 122 (1906).
22 Haber & Mitland, Zeit. Electrokem, 13, 309, (1907).
23 Manchot. Ber. 42, 4942.
24 W. J. Muller, Zeit. Electrochem, 15, 696.
25 Kruger, Zeit. Physikal Chem., 39, 104, (1902).
26 Fredenhagen, Zeit. Physikal Chem., 43, 1, (1903) and 63, 1, (1908).
28 E. Grave, Zeit., physikal. chem., (1911), 77, 513.
27 Foerster, Abhandlunge der Bunsen Ges., No. 2, (1902).
29 Sackur, Zeit. Electro Chem., (1908), 14, 607.
30 Le Blanc, Lehrbuch der Electrochemie.

AUTOBIOGRAPHY.

The writer was born at Leadville, Colorado, and received his early education in the public schools of Illinois. He received the Bachelor of Science degree at Northwestern University in 1911. The two following years were spent as a graduate assistant at the University of Washington, the degree of Master of Arts being granted in June, 1913. Through the aid of Loretta Denny fellowships work was continued in the same institution during the years 1913-1915.